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QUARTERLY LETTER REPORT
COVERING
October 1, 1963 - December 31, 1963

THERMODYNAMIC PROPERTIES
OF
BIMETALLIC COMPOUNDS

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Submitted to:

Advanced Research Projects Agency
The Pentagon, Room 3D-159
Washington 25, D. C.

Attn: Advanced Propellant
Chemistry Office

December 31, 1963

MAJOR ACCOMPLISHMENTS

On November 15, work on the follow-on program was initiated. The objectives of the follow-on program differ from those of the previous contract as they seek the determination of the heat of formation of the chlorides, fluorides, and oxides of boron and beryllium by solution calorimetric techniques. The final phase under the previous contract was devoted towards the assembly of a fluorine combustion method for calorimetric measurements.

A. Fluorine Combustion Calorimeter

Prior to the beginning of this period, the fluorine combustion system was passivated and readied for the combustion studies of metallic materials. During this last period, techniques were worked out to enable the charging of the bomb at various fluorine pressures, and involved the manipulation of liquid and/or gaseous fluorine in a tight manifold. As part of this study to determine the heat of formation of AlB_2 by fluorine combustion, it was also necessary to establish a satisfactory furnace configuration within the bomb which would withstand the energetic combustion. The configuration adopted utilized CaF_2 coated alumina discs and crucibles, and was found to withstand the thermal shock without shattering.

The material purchased as AlB_2 was found to be AlB_{12} plus aluminum. The aluminum was removed and the AlB_{12} was used in

these initial combustion studies, although the heat of formation of AlB_{12} was not being sought. Combustions were carried out at various pressures of fluorine with boron and AlB_{12} in the form of loose powders and again as pellets containing various portions of teflon powder. The teflon powder enabled the material to be pelletized and aided ignition.

The conditions which yielded nearly 100% combustion (by visual observation) of the products and unburnt sample required a fluorine pressure of 125 psig and a material to teflon ratio of 1 to 4.

Although no quantitative thermochemical data were generated on the AlB_{12} system, the fluorine combustion method of calorimetric study was developed to a point where quantitative studies are possible.

B. Solution Calorimeter

A silvered, dewar-type reaction vessel was assembled in which the heats of solution of B_2O_3, (glassy and crystalline), H_3BO_3, BCl_3, and BF_3 will be measured. From these measurements, the heats of formation of B_2O_3, (glassy and crystalline), BCl_3, and BF_3 will be calculated. Initial preliminary runs indicate that an adiabatic approach will improve the accuracy of this measurement. A technique has been developed to enable this to be done with our immersed dewar, in which the relatively fast reaction takes place. Simulation runs are in progress and those are to be followed by the electrical calibrations.

A drying vacuum furnace has been assembled to dry our oxides and boric acid, and also to prepare our glassy boron oxide.

The first measurements will be the heat of hydrolysis of crystalline B_2O_3.

During this period presentations of the work generated in this program were given at the Annual Calorimetry Conference, October 16-18, Bartlesville, Oklahoma, and at the JANAF Thermochemical Panel Meeting, November 5-7, New York City.

PROBLEMS ENCOUNTERED

None

ACTION REQUIRED BY ARPA

None

FUTURE PLANS

Under the follow-on program, several of the oxides, fluorides and chlorides of boron and beryllium will be studied thermochemically to determine their heats of formation. The solution calorimetry method will be employed.